ORIGINAL ARTICLE

Adsorption of benzene from benzene/n-C$_6$ and n-C$_7$ mixture by nano Beta zeolite with different Si/Al ratios

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Abstract   The adsorption of benzene from benzene/n-alkane mixtures was studied by two types of nano Beta zeolite with Si/Al ratios of 11.5 and 24.5. Benzene was adsorbed into benzene/n-hexane and n-heptane mixtures which had 0.5% up to 10% mole fraction of benzene using batch technique in the ambient temperature. The nano Beta zeolite has active sites on its surface, which have interaction with π electron in benzene, and this can increase the heat of adsorption. The Si/Al ratio defines the number of active sites in the zeolite surface and the heat of adsorption. However, an increase in the active sites of Beta zeolite declines the entropy of adsorption. Therefore, free energy of mixing specifies the potential of adsorption in Beta zeolite.

   As the results indicated in all mixtures, benzene is adsorbed more than n-hexane and n-heptane into the Beta zeolite surface, which suggests that this type of zeolite has a high separation factor (∼50) for benzene in Beta zeolite (Si/Al = 24.5). Also, Beta zeolite with Si/Al = 24.5 had a greater separation factor than Beta zeolite with Si/Al = 11.5 in similar mixtures.

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1. Introduction

Nowadays, improving the gasoline quality is one of the most important environmental concerns, which can be done through the isomerization of straight chain paraffins and the removable aromatics gasoline. The isomerization reaction is done on the normal alkanes in the branch isomers that increase the octane number of gasoline. Also, aromatics are removed by adsorption or hydrogenation (Weyda and Kohler, 2003; Chica et al., 2001; Mao et al., 2000; Nikolaou et al., 2004).

   Y (FAU), X (FAU), Beta (BEA), and other zeolites can adsorb the aromatics from the aromatic/alkane mixtures and are used for the isomerisation of n-paraffins. The pore size of these zeolites are classified as large size (6.5–7.5 Å) which is greater than some of n-alkane and aromatic molecules, so aromatics can permeate through the zeolite pores. Moreover, the active sites on the zeolite surface can interact with the π

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electrons of aromatics, and this will lead to a higher heat of adsorption for the aromatics. There are some studies which worked on adsorption of different aromatics from aromatic/alkane and alkene mixtures. They investigated the effect of zeolite type on aromatic separation factor (Anabtawi et al., 1996; Yonli et al., 2009; Fathizadeh and Nikazar, 2009).

In gas and liquid phase, the aromatic adsorption from the aromatic/alkane mixture by the Na-Y and Na-X zeolite was investigated by Fathizadeh and Nikazar (2009); Daems et al. (2005), and Yu et al. (2006). The separation factor was reported to be greater than 150 in these works. In addition, aromatics are preferentially adsorbed from n-hexane, n-heptane and n-octane mixtures because aromatics have higher heat of adsorption and active site more efficiently in the NaY super cages (Fathizadeh and Nikazar, 2009; Yu et al., 2006; Zhang et al., 2008; Yu et al., 2005). However, in the case of Beta zeolite, there are no published data concerning the adsorption of aromatics from aromatic/alkane mixtures in the liquid phase, which can help in better understanding of its adsorption behavior in Beta zeolite.

Beta Zeolite is a crystalline synthetic aluminosilicate with large micropores, three-dimensional interconnecting channels with 12-member rings and a Si/Al ratio from 5 to 100. It is one of the best catalysts for n-heptane because of its large pore size (7.6 A°) (Chica and Corma, 1999; Krishna, 2001; Krishna et al., 2002a, b). Benzene ($0.69 \times 0.62 \times 0.34$ nm^3) is larger than n-C$_6$ ($0.75 \times 0.42 \times 0.42$ nm^3) and n-C$_7$ ($0.88 \times 0.42 \times 0.42$ nm^3); therefore, normal hydrocarbon can permeate into the zeolite pores easier than benzene. Also, the powerful interaction between benzene and active sites leads to an appropriate separation factor (Bellata et al., 1997; Chica and Corma, 1999; Krishna et al., 2002a, b).

In this paper, first, the nano Beta zeolite with different Si/Al ratios was synthesized and characterized by X-ray diffraction (XRD) and temperature programed desorption (TPD). Secondly, the separation factor of benzene from benzene/n-C$_6$ and n-C$_7$ mixtures was studied in the liquid phase using the batch adsorption techniques over the nano Beta zeolite. Also, the effect of Si/Al ratios, benzene concentrations and the size of the n-alkanes were thoroughly investigated. Finally, the results were fitted into two isotherms and the parameters of these isotherms were calculated.

2. Experimental

2.1. Beta zeolite preparation

Nano Beta zeolites were synthesized hydrothermally by tetra ethyl ammonium hydroxide (TEAOH) as the template.

0.53 g of sodium chloride with 1.44 g of potassium chloride was added to 179.2 g of a tetra ethyl ammonium hydroxide solution (TEAOH, Fluka, 40 wt% aqueous solution) and the mixture was stirred for 10 min. Subsequently, 29.54 g of Aerosil (Silica source, Degussa 380, 99 + %) was added to the mixture with vigorous stirring (Solution A). In the next step, 0.33 g of sodium hydroxide and (1.7 g, 3.45 g) sodium aluminate were dissolved in 5 g of deionized water (Solution B). Solution B was added dropwise to Solution A with continuous stirring until a uniform solution was formed. The homogenized gel was then loaded into a PTFE lined autoclave. The autoclave was sealed with a stainless steel cover and placed into a rotary oven. Heating was provided for 48 h at 140 °C (at 60 rpm). The crystallization process was terminated by quenching the autoclave in cold water. The synthesized powders were recovered by centrifugation. The powders were washed with hot deionized water several times so that the pH of rinsed water decreased to about 9. The washed powders were dried at 100 °C overnight. In order to remove the existing organic components from the powders, the zeolite was calcined at 550 °C for 2 h in nitrogen atmosphere and continued for 2 h in air. Zeolites with ammonia content were prepared by cation exchange process using 0.3 N NH$_4$Cl solution at 80 °C. The process was repeated two times. NH$_4$-Beta forms of zeolite were washed with deionized water and dried at 70 °C overnight. Ammonia was then removed from the zeolite by heating at 550 °C for 4 h which yields H-Beta zeolite (Talebi et al., 2008; Nikolaou et al., 2004).

2.2. Zeolite characterization

Powders' X-ray diffraction (XRD) patterns were obtained using a Philips (model PC-APD) diffractometer applying Cu kα radiation at 40 kV and 30 mA (Fig. 1a and b). The results of the XRD test showed that two different Si/Al ratios of Beta zeolite were synthesized. Also, the average crystal dimension of Beta zeolite can be calculated using Scherrer's equation from the XRD test. Temperature programed desorption (TPD) was carried out using MICROMERITICS 2900 TPD/TPR. Protonated zeolite samples were flushed by inert gas (He) with 30 ml/min flow rate for about 45 min at 500 °C. Samples were cooled down to 100 °C by passing ammonia over the latter one for 30 min with a flow rate of 30 ml/min. Inert gas was applied to remove the physisorbed ammonia molecules. In the case of TPD experiments, the samples were heated from 100 °C to 500 °C with a rate of 10 °C/min, and the desorbing species were monitored and measured simultaneously using a TCD detector.
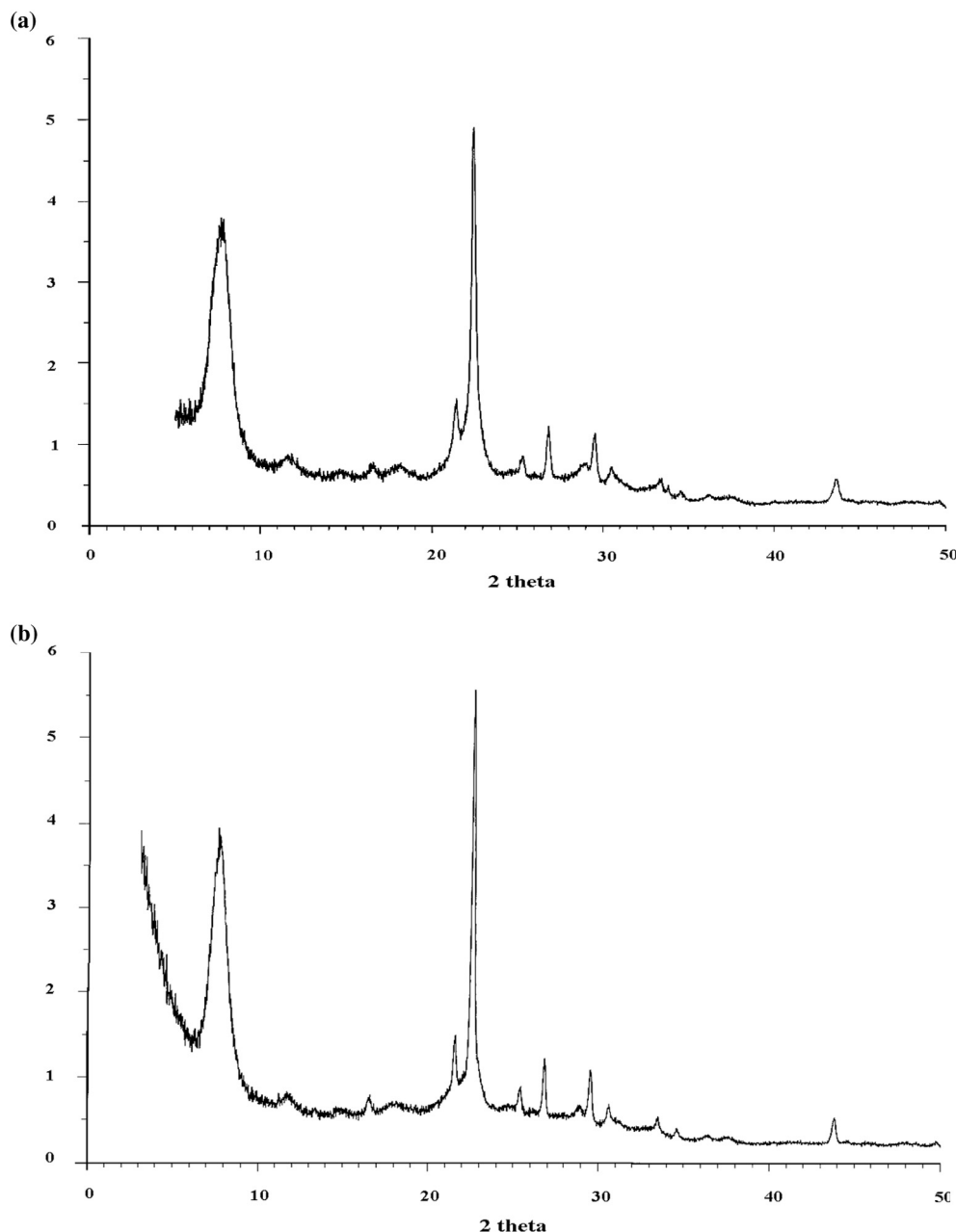
(a)

(b)

Figure 1 (a) XRD pattern (11.65) and (b) XRD pattern (24.5).

2.3. Adsorption isotherm for benzene/n-alkenes

In this section, the adsorption's experimental data of benzene/n-alkane are fitted into two isotherms. Langmuir and Freundlich adsorption isotherm models are defined as:

$$q_i = K_i x_i^n \quad \text{Freundlich adsorption isotherm} \quad (4)$$

$$\frac{q_i}{q_m} = \frac{K_i x_i}{1 + K_i x_i} \quad \text{Langmuir adsorption isotherm} \quad (5)$$

where q_i (mol/g) is the amount of moles adsorbed to component i, K_i is the adsorption constant of component i, and x_i (mol%) is the moment concentration of component i. In the Langmuir isotherm, the q_m (mol/g) is defined as the monolayer sorption capacity and the Langmuir constant K_i is the sorption energy. In the Freundlich adsorption isotherm, the q_m and K_i are given from the slope and intercept via the plot of x_i/q_i versus x_i, respectively. Also, the values of n and K_i in the Langmuir isotherm are calculated from the slope and the intercept via the plot of Ln(q_i) against Ln(x_i), respectively. Table 3 shows the results of both Langmuir and Freundlich adsorption constants at different components of the benzene/n-alkane. Also, the fitted equilibrium data for both isotherm models are shown in Fig. 3.

In Beta zeolite with Si/Al = 11.65, all parameters of both isotherms decreased as n-alkane change from n-C$_6$ to n-C$_7$, but Beta zeolite with Si/Al = 24.5 has a different situation
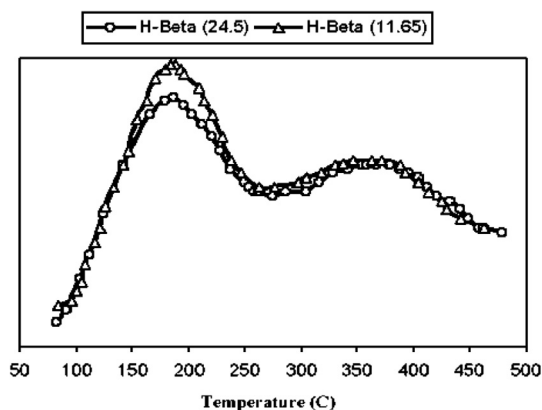
Figure 2   NH$_3$ TPD of two zeolite samples.

with Si/Al = 11.65. The q_m and n increased and K_i decreased while the number of carbon increased in n-alkane. Fig. 3 shows that the Langmuir isotherm had the best fitting for benzene adsorption from benzene/n-alkane mixtures.

2.4. Adsorption process

A batch technique was used for determining the competitive adsorption of benzene and alkane equilibrium in liquid phase. In this method, Zeolite samples (0.3 g) were put into 10 ml glass vials and slowly heated (0.5 °C/min) until the temperature reached 350 °C and held constant overnight. All water and impurities present inside the zeolite pores were removed in condition, and then vials were immediately sealed in order to avoid the water uptake after the regeneration. After weighing the regenerated zeolite, the binary mixture of benzene/n-hexane and n-heptane was added into the zeolite containing vials, while vial weight increased to 1.3 g, to be used as a blank. Samples were stirred continuously at the ambient temperature for 24 h duration, and then they were analyzed in a gas chromatograph (GC) with FID detector. A fused silica column (50 m × 250 μm × 0.4 μm) was used to determine the composition of all blanks and samples.

The amount of adsorbed aromatics at zeolite pores was calculated via the mass balance:

$$q_{aromatic} = \frac{(\text{wt}\%_{ba\ln k} \times M_{L,0}) - \text{wt}\%_{sample} \times M_{L,A}}{m_{zeolite} \times 100} \quad (1)$$

where wt$\%_{blank}$ and wt$\%_{sample}$ are the concentration (wt%) of the aromatic in the non-adsorptive liquid phase before and after adsorption.

$$M_{L,A} = M_{L,0} - 0.23 \times m_{zeolite} \times \rho_{av} \quad (2)$$

Also, $M_{L,0}$ is the total mass of liquid added to the zeolite before adsorption; $M_{L,A}$ is the mass of the non-adsorptive liquid after the adsorption; $m_{zeolite}$ is the regenerated zeolite mass; ρ_{av} is the average density of the sorbate in pores at room temperature. The change in the mass of the non-adsorptive liquid phase due to its partial uptake inside the zeolite pores is corrected with formula (2). The factor 0.23 is the volume per unit mass of zeolite.

The selectivity factor between aromatic and n-alkane was calculated as follows:
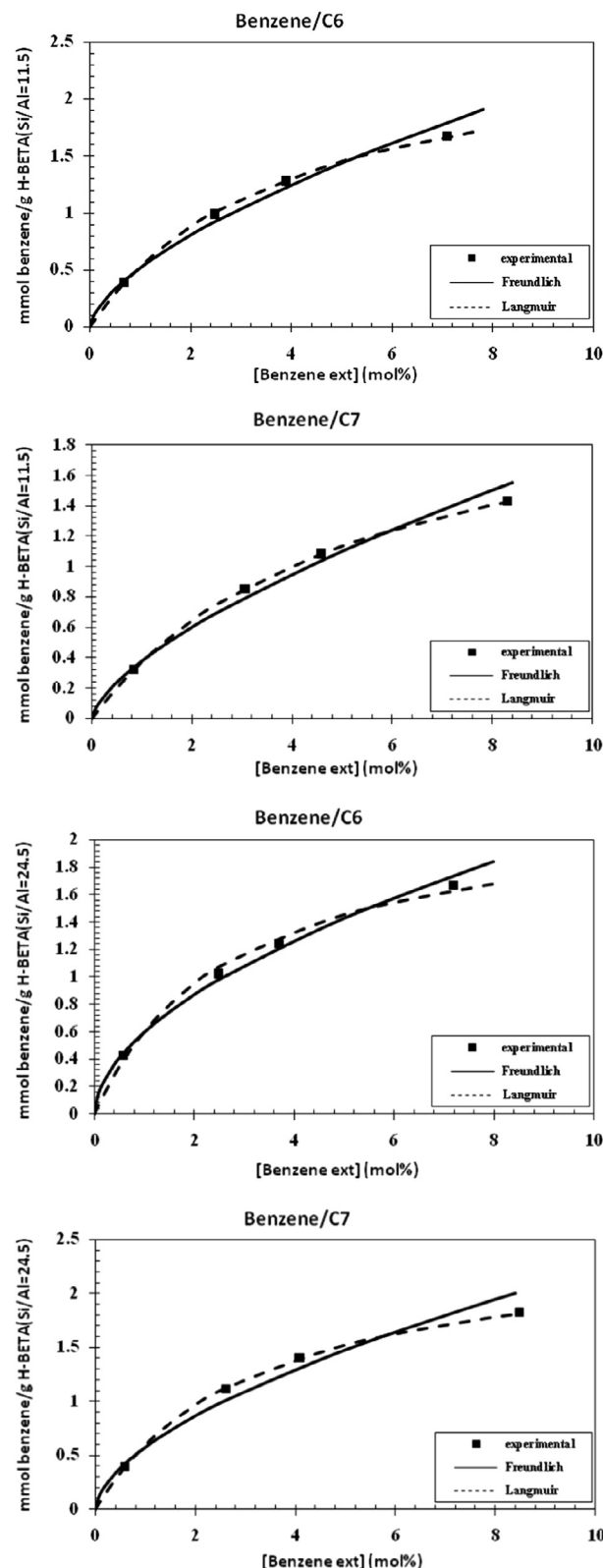

Figure 3   Experimental and fitted adsorption isotherms of benzene in n-alkanes (hexane and heptanes) adsorbed on Beta zeolite in liquid phase (experimental data: symbols; Langmuir model (- - -) and Freundlich (—)).

Table 1   Acid strength and distribution in two zeolite samples.

Zeolite sample	Total acid (μmol/g)	Weak acid (μmol/g (°C))	Strong acid (μmol/g (°C))
B (11.65)^{A0}	862	653(197)	209(363)
B (24.5)^{B0}	786	591(196)	191(358)

Table 2   Benzene/n-alkane mixture adsorption on Beta zeolite at 295 ± 0.5 K.

Benzene liquid concentration (mol%) in Si/Al = 11.65	Benzene/n-alkane adsorption selectivity	Benzene liquid concentration (mol%) in Si/Al = 24.5	Benzene/n-alkane adsorption selectivity
Benzene/n-C$_6$			
0.68	35.09	0.57	47
2.47	32.91	2.49	34.33
3.89	32.37	3.69	32.19
7.08	31.53	7.19	30.86
Benzene/n-C$_7$			
0.84	25.57	0.59	46.23
3.05	23.55	2.6	42.3
4.57	22.52	4.07	41.4
8.28	20.31	8.48	37.31

Table 3   Langmuir and Freundlich adsorption constants.

Mixture of benzene in Si/Al = 11.65	Langmuir		Freundlich		Mixture of benzene in Si/Al = 24.5	Langmuir		Freundlich	
	K_i	q_m (10^{-3})	K_i	n		K_i	q_m (10^{-3})	K_i	n
n-C$_6$	0.256	2.59	0.52	0.634	n-C$_6$	0.363	2.258	0.596	0.542
n-C$_7$	0.192	2.33	0.38	0.661	n-C$_7$	0.317	2.429	0.576	0.586

$$\alpha_{ij} = (q_i/q_j) \times (C_j/C_i) \qquad (3)$$

where q_i and q_j are the amount of (mol/g) aromatic and n-alkane adsorbed, C_i and C_j are the concentration of benzene and n-alkane (mol/l) present in the non-adsorptive liquid phase at equilibrium (Fathizadeh and Nikazar, 2009; Daems et al., 2005).

3. Results and discussion

3.1. Beta zeolite characterization

The crystallinity and phase purity of the fabricated beta zeolite samples were investigated by the XRD pattern (Fig. 1). The Beta structure has a series of peaks at 7.6, 13.4, 14.4, 21.2, and 22.2 in the XRD pattern which can be seen in synthesized Beta zeolite samples. Results show that the XRD patterns of the Beta zeolites are in agreement with standard XRD pattern of Beta zeolite (Zhang et al., 2008). The XRD pattern result depicted that the average size of these Beta zeolites was between 100 and 200 nm which was calculated by Scherrer's equation. Also, the results of the acidity measurements and ammonia TPD are shown in Table 1 and Fig. 2, respectively. The more total acidic site can be seen in nano beta zeolite with Si/Al = 11.5 which shows an inverse relationship between the active site and Si/Al ratio at zeolites (Fathizadeh and Nikazar, 2009).

3.2. N-alkane/benzene adsorption

Table 2 shows the separation factor of benzene in the two different nano Beta zeolites (with Si/Al = 11.65 and 24.5) as benzene concentration in the mixture is below 10 mol%. Benzene is advantageously adsorbed at both nano Beta zeolites and has a separation factor higher than 25. The minimum of separation factor was obtained in the highest concentration benzene and lowest Si/Al ratio (Benzene/n-C$_7$ = 8.28%). In the same mixtures, the separation factor of benzene increased as the Si/Al ratio raised from 11.5 to 24.5. Also, the power of benzene adsorption improved with reducing the benzene concentration in the all samples.

In zeolite with Si/Al = 11.65, the adsorption selectivity is topically less than the zeolite with Si/Al = 24.5 in the same concentration of benzene. Also, the results show that the maximum separation factors of benzene happen in the benzene/n-C$_6$ mixtures. Therefore, it can be said that the entropy of adsorption has important roles in the benzene/n-C$_6$ mixtures. The benzene adsorption was less sensitive to benzene concentration on the Si/Al = 11.65.

The separation factor in nano Beta zeolite with Si/Al = 24.5 is higher than Beta zeolite with Si/Al = 11.65. The adsorption selectivity decreased as the carbon number of the n-alkane increased. Also, the adsorption selectivity decreased significantly at benzene/n-C$_6$ mixtures which have

Table 4 The adsorption heat of n-hexane and n-heptane on beta zeolite (Makowski and Ogorzalek, 2007).

Molecule	Heat of adsorption (kJ mol^{-1})	Entropy of adsorption (J mol^{-1} K^{-1})
n-Hexane	53	85
n-Heptane	61	90

the biggest separation factor of all mixtures and this treatment is more sensitive to the low concentration of benzene.

3.3. Pore size and active site

In Beta zeolite, the pore sizes are larger than the diameter of n-alkane and benzene; therefore these hydrocarbons can penetrate inside of the Beta zeolite pore. These n-alkanes (n-C$_6$ and n-C$_7$) have better permeation than benzene which did not mainly control the adsorption system and increased the rate of n-alkane adsorption. In fact, pore size is not the main parameter in benzene/n-alkane adsorption.

In other words, the surface of Beta zeolite has a positive active site which is related to the Si/Al ratio. These active sites interact with π electron of benzene and increase the heat of the adsorption in benzene; therefore, benzene was adsorbed better than n-alkanes into the Beta zeolite surface. Table 2 shows that Beta zeolite better adsorbed benzene and has the separation factor $> \sim 20$. Active sites are increased via a decreased Si/Al ratio in Beta zeolite which increased the heat of adsorption difference of benzene and n-alkane but decreased the entropy of adsorption for benzene. Increased enthalpy and decreased entropy lead to the declined free energy of mixing. Therefore, the separation factor in Beta zeolite with Si/Al = 24.5 is higher than zeolite with Si/Al = 11.5.

Also, n-heptane has the higher heat of adsorption than n-hexane in Beta zeolite, because n-heptane has more contact surface with zeolite than n-hexane (Table 4). Therefore, the separation factor is much higher for benzene/n-C$_6$ mixture than benzene/n-C$_7$ mixture in Beta zeolite with Si/Al = 11.65, which is inverse in nano Beta zeolite with Si/Al = 24.5. The entropy of adsorption is more effective than the heat of adsorption in nano Beta zeolite with the highest Si/Al ratio. Therefore, the separation factor of benzene/n-C$_7$ mixture in nano Beta zeolite with Si/Al = 24.5 is higher than benzene/n-C$_6$ mixture. In benzene/n-C$_6$ mixture of Beta zeolite, Si/Al = 24.5, the difference of mixing free energy between benzene and n-hexane is so high that has increased the separation factor. Also, this separation factor is more sensitive to benzene concentration.

3.4. Adsorption isotherms

The generated adsorption isotherms (solid and discrete lines) nicely fit the experimental results (symbols). The Langmuir isotherm curve has a good fitting with the experimental data in all mixtures, but the Freundlich has a very small error in high concentration of benzene, which is still acceptable. In the Langmuir isotherm, the rate of adsorption depends on the free active sites in adsorbent surface. Also, the molecules of benzene have been adsorbed into Beta zeolite surface active sites.

Therefore, the Langmuir isotherm has good prediction of benzene adsorption into Beta zeolite.

The Freundlich isotherm is based on the polynomial equation, and disregards occupation active sites on Beta zeolite surface, which lead to the small error between curve and experimental. When the power of this isotherm (n) is the least, the separation factor is sensitive to the concentration which illustrates benzene/n-C$_6$ in Beta zeolite with Si/Al = 24.5 on Table 2.

4. Conclusions

The experimental data show that nano Beta zeolite adsorbs benzene better than n-alkanes, because benzene has a higher heat of adsorption and higher entropy of adsorption in this zeolite. Also, a decreasing Si/Al ratio caused the decline of the separation factor. Benzene is adsorbed into the nano Beta zeolite with Si/Al = 24.5 from benzene/n-C$_6$ mixtures; the adsorption selectivity was as high as 50. The separation factor in nano Beta zeolite is influenced by the Si/Al ratio, the type of n-alkane, and the concentration of benzene in the mixture. The selectivity of benzene from benzene/n-C$_7$ mixture in nano Beta zeolite with Si/Al = 11.65 is lower than nano Beta zeolite with Si/Al = 24.5; even though nano Beta zeolite with Si/Al = 11.65 has higher heat of adsorption. Enthalpy of adsorption leads to the high adsorption of benzene in nano Beta zeolite with Si/Al = 24.5.

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